Pulse Radiolysis with Electric Conductivity. A Method of Obtaining the Rates of Propagation in the Radiation-induced Polymerization of α-Methylstyrene*[1]

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(Received June 24, 1969)

The present authors previously studied intermediates in irradiated dry α-methylstyrene by means of pulse radiolysis with optical absorption measurements.(1) Following that work, similar studies have been reported by Swallow and Schneider(2) and by Metz and his coworkers(3) for styrene as well as α-methylstyrene. All three groups agreed that one of the intermediates is the anion radical of these compounds. Now we wish to report on further investigations in which we applied a method of electric conductivity measurements after a pulse irradiation in order to obtain the rates of propagation in the reaction. The method is, in principle, similar to that used for determining the mobilities of a carrier in semiconductors(4) and later applied to the studies of radiation chemistry by Hummel and Allen(5) in order to obtain the yield of ions in some liquid hydrocarbons.

As is shown in Fig. 1, a very thin layer of ions, both anion and cation, is produced by a single pulse of X-rays in a sample very close to one electrode, E_1, which is negatively polarized in the present case. The cation then discharges on the electrode immediately after its formation, while the anion moves to the other electrode, E_2, for measurements over rather a long period of time. In this way, the mobility of anion can, in principle, be measured separately. The mobility of the cation can also be measured by simply reversing the polarity of E_1. When a polymerizing system is studied, an anion, or an anion radical, will polymerize as it moves to E_2. Since the diffusion constant, or the mobility, of ions generally decreases as their molecular weights increase, we can compare the rate of the propagation of anionic species directly with that of cationic species by comparing the respective measured mobilities by just changing the polarity of E_1. An example of such measurements is shown in Fig. 2.

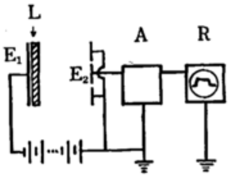

Fig. 1. The diagram of mobility measurements. E_1, E_2; electrode, L; layer of ions, A; ammeter and R; recorder.

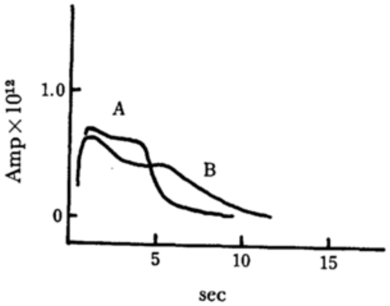

Fig. 2. The current-time curves with dry α-methylstyrene. A, positive ions and B, negative ions.

TABLE 1. THE MOBILITIES OF IONS IN α-METHYLSTYRENE $[\mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{sec}^{-1}]\times10^4$

Cation	Anion	Condition
5.0	1.9—1.4	dry[G(-monomer)$\geq$7300]
5.0	4.0	saturated with water

Some data on mobility thus obtained in α-methylstyrene are given in Table 1. From these data and from the fact that the polymerization proceeds much faster in a dry sample than in wet ones,(6) it may be concluded that the anionic reaction is more important than the cationic one in the radiation-induced polymerization of α-methylstyrene.

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*[1] Presented at the 9th Japan Conference on Radioisotopes, Tokyo, May, 1969.

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